The V International AMMCS
Interdisciplinary Conference
Waterloo, Ontario, Canada
18-05-2019

Differential capacitance of ionic liquid interface with graphene: the effects of correlation and finite size of ions

A. Shalabi[1], L. Daniels[2]

[1] *Department of Physics and Astronomy, University of Waterloo, Waterloo, Canada, ashalabi@uwaterloo.ca*
[2] *Department of Applied Mathematics, University of Waterloo, Waterloo, Canada, lm2danie@uwaterloo.ca*

Graphene has shown great potential for applications in biological and chemical sensing due to its unique electronic band structure [1, 2]. Graphene based sensors typically operate as Field Effective Transistors with the graphene layer operating as the conducting channel with an electrolyte solution as its gate [3]. Recently, there has been a peak in interest in studying the electric double layer that arises at the interface of doped graphene and a class of electrolytes known as ionic liquids. Ionic liquids are a class of ionic salts that are molten at room temperature with low volatility and high ionic concentration[4, 5], and are characterized by the overscreening and overcrowding effects in their electric double layer [6].

In this work, a mean field model for ionic liquids is presented. This model takes into account both the ion correlation and the finite ion size effects. A computational procedure has been developed in order to calculate the differential capacitance of the ionic liquid interface with single-layer graphene. The role of the ion packing on the transition from Camel to Bell shapes in the diffuse layer is analyzed. Next, the effect of the ion packing fraction and the correlation lengths on the fraction of the potential that goes into charging the graphene electrode is analyzed. In addition, we explore small packing fractions in the dilute electrolyte regime and we extended those results for asymmetric ionic liquids. We show that the main effect of a graphene electrode versus a metallic one arises due to a V-shaped minimum in its quantum capacitance due to the Dirac cone structure of graphene's π electron bands. Consequently, the total interfacial capacitance exhibits a Camel-shaped dependence on the potential applied to the system, even for large ion packing fractions and finite correlation lengths.

References

[1] L. H. Hess, M. Seifert and J. A. Garrido, *Graphene Transistors for Bioelectronics,* in Proceedings of the IEEE, **101, no. 7**, pp. 1780-1792 (2013).

[2] S. Chen, Z. B. Zhang, L. Ma, P. Ahlberg, Z. Gao, Z. Qiu, D. Wu, W. Ren, H. M. Cheng, S. L. Zhang, *A graphene field-effective capacitor sensor in electrolyte,* Applied Phys. Lett. **101** (2012) 154106.

[3] P. Sharma and Z. L. Miskovic. *Capacitance of graphene in aqueous electrolytes: The effects of dielectric saturation of water and finite size of ions*, Phys. Rev. B, **90** pp.125415 (2014).

[4] Maxim V. Fedorov and Alexei A. Kornyshev. *Ionic Liquids at Electrified Interfaces*, Chemical Reviews **114** pp. 2283-2307 (2014).

[5] Silvester, D. Compton, R. *Electrochemistry in Room Temperature Ionic Liquids: A Review and Some Possible Applications,* Zeitschrift fur Physikalische Chemie, **220(10)** pp. 1247-1274 (2009).

[6] Martin Z. Bazant, Brian D. Storey, and Alexei A. Kornyshev, *Double Layer in Ionic Liquids: Overscreening versus Crowding*, Phys. Rev. Lett. **106**, 046102 (2011).